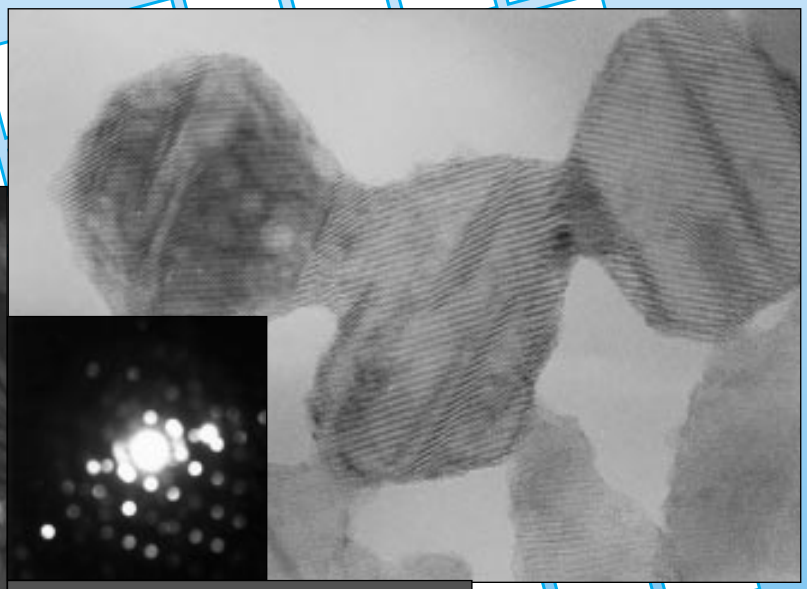
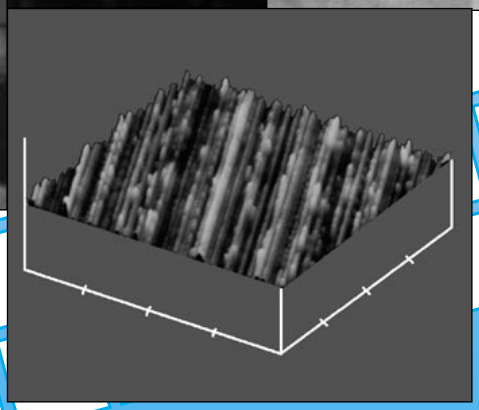
Materials Characterization

Chemistry & Materials Science Directorate





University of California
Lawrence Livermore National Laboratory

About Our Materials Characterization Labs

The Chemistry and Materials Science Directorate at Lawrence Livermore National Laboratory operates materials characterization laboratories that provide specialized services to a wide variety of Laboratory programs. Our expert technical staff is also available for data interpretation and assistance with problem solving. Measurements, analysis, and consultation can be done quickly for urgent cases. Charges for these services are based on a recharge system providing reliable cost estimation and recovery, and in some laboratories, qualified users can perform their own measurements by paying a user fee based on the cost of supervision, maintenance, assurances, and other operating and support costs for the facilities. In addition to the dedicated service facilities identified here, our Directorate has many materials research facilities that can be used in response to requests for more demanding or specialized services and collaboration.

Materials Characterization

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The Technologies

Surface Analysis

For complementary surface, depth-profile, thin-film, and interface analysis, we provide qualitative and quantitative compositional information and chemical bonding information using well-known techniques such as Auger electron spectroscopy (AES), secondary ion mass spectroscopy (SIMS), x-ray photoelectron spectroscopy (XPS), and Rutherford backscattering (RBS), as well as less common methods such as atomic force microscopy (AFM) and scanning tunneling microscopy (STM), particle-induced x-ray emission (PIXE), nuclear reaction analysis (NRA), and forward recoil spectroscopy (FRS). Choices of probe size can be as small as 40 nm with sensitivities to 10 ppm, depending on the method. Additionally, surface topography can be examined by STM or PIXE.

Electron Microscopy

For information about internal microstructure, surface topography, and defects, we use the electron microscopic techniques of scanning electron microscopy (SEM), electron microprobe analysis (EMP), and transmission electron microscopy (TEM) to obtain high-resolution images atomically with resolution to 0.18 nm and topographically to 2 nm. Elemental composition and crystalline phase determination are obtained quantitatively for elements heavier than boron over areas as small as 2 nm using energy dispersive spectroscopy (EDS) or wavelength dispersive spectroscopy (WDS). TEM also provides atomic structure and electronic structure information with microdiffraction and parallel electron energy-loss spectroscopy (PEELS).

X-Ray Analysis

For structural analysis of crystalline and multilayer materials, a variety of diffraction techniques provide information about crystal structure, chemical bonding, nearest-neighbor distances, atomic arrangements, and orientation. Methods available include x-ray diffractometry (XRD), time-resolved x-ray diffractometry (TRXRD), extended x-ray absorption fine structure (EXAFS), and x-ray absorption near edge structure (XANES), with penetrations from bulk to monolayer and probe sizes to a few micrometers.

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Characterization Quick-Check Guide

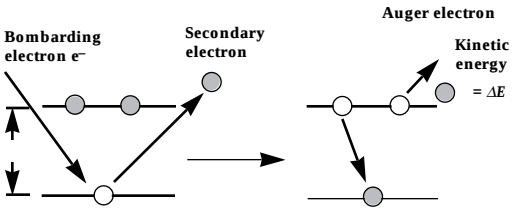
Technique/Main uses	Elemental	Chemical state	Phase	Defects	Structure	Image	Typical depth and width probed	Trace capability (sensitivity)
	Type of information							
Complementary surface, thin film, and interface analysis								
Auger electron spectroscopy (AES)								
Semiquantitative elemental composition of inorganic materials using electrons; good depth resolution	✔	✔				✔	5-nm depth 40-nm width	0.1%
Secondary ion mass spectroscopy (SIMS)								
Qualitative composition and detection of trace-level impurities as a function of depth; destructive but higher absolute sensitivity; detects hydrogen and helium	✔					✔	5-nm depth 1-μm width	ppb–ppm
X-ray photoelectron spectroscopy (XPS)								
Semiquantitative elemental composition using x rays with lower lateral spatial resolution; chemical information from comparison with atlas	✔	✔					5-nm depth 200-μm width	Not a trace-element method
Rutherford backscattering (RBS)								
Quantitative composition and nondestructive depth profiling; crystal damage information	✔			✔	✔		5-μm depth Millimeter width	0.001–10 at.%
Particle-induced x-ray emission (PIXE)								
Fast analysis for many elements, in all materials, simultaneously; background lower than EDS, EMP, so trace peaks more resolved; better for thin films	✔			✔	✔		5-μm depth Millimeter width	0.0001–10 at.%
Nuclear reaction analysis (NRA)								
Quantitative high-resolution depth profiles of light elements ($Z \geq 15$); isotope selectivity	✔			✔	✔		5-μm depth Millimeter width	0.0001–10 at.%
Forward recoil spectroscopy (FRS)								
Quantitative depth profiles of light elements (particularly hydrogen)	✔			✔	✔		2-μm depth Millimeter width	0.01–1 at.%
Other surface or near-surface analysis								
Scanning tunneling microscopy (STM) & Atomic force microscopy (AFM)								
3-D imaging in air, vacuum, and solution with atomic resolution; also imaging of non-conductors; hardness and elastic modeling by nano-indentation			✔	✔		✔	0.01–0.1Å depth Atomic width	—

Technique/Main uses	Type of information: Elemental	Chemical state	Phase	Defects	Structure	Image	Typical depth and width probed	Trace capability (sensitivity)
Electron microscopy								
Scanning electron microscopy (SEM)								
Topographic imaging; semiquantitative elemental composition using EDS	✔			✔		✔	2-µm depth 10-nm width	1%
Electron microprobe analysis (EMP)								
Quantitative elemental or compound analysis; compositional mapping and imaging; maximum sensitivity with high beam current and better peak resolution using WDS	✔					✔	1-µm depth 0.5-µm width	0.5%
Transmission electron microscopy (TEM)								
Microstructural imaging, atomic structure, and microchemical analysis from small regions			✔	✔	✔	✔	100-nm depth 2-nm width	0.5–2%
Energy dispersive spectroscopy (EDS)								
Quantitative analysis with high spatial resolution; may have peak overlap, x-ray absorption, or fluorescence problems	✔					✔	100-nm depth 2-nm width	0.5–2%
Parallel electron energy-loss spectroscopy (PEELS)								
Quantitative, local, elemental concentration; electronic and chemical structure; nearest neighbor atomic spacing analysis	✔	✔					60-nm depth 20-nm width	1%
X-ray analysis								
X-ray diffractometry (XRD)								
Crystalline phase and structural properties identification; concentration profiles; defect characterization; thickness measurements			✔	✔		✔	10-µm depth Millimeter width	3%
Time-resolved x-ray diffractometry (TRXRD)								
Real-time in situ monitoring of phase transformations and chemical dynamics			✔		✔		10-µm depth Millimeter width	1%
Extended x-ray absorption fine structure (EXAFS) & X-ray absorption near-edge structure (XANES)								
Local structural distribution of atoms; chemical bonding information; surface structure and chemistry	✔	✔	✔		✔		10-µm depth (solids) Millimeter width	1%

Auger Electron Spectroscopy

- **Surface-sensitive technique (0.5- to 5-nm analysis depth)**
- **Depth profiling**
- **Semiquantitative detection of all elements except hydrogen and helium**
- **Area, point, or line scans with spatial resolution to 50 nm**
- **Two-dimensional maps of elemental distribution**
- **Ultra-high vacuum fracture of samples at room or liquid nitrogen temperature**
- **Secondary electron and backscattered electron photos of sample**

The sample is irradiated with a primary electron beam (0.5 to 20 kV) that ejects a core-level electron. An outer-shell electron fills this core-level vacancy, transferring energy to a third (Auger) electron. The Auger electron escapes with a kinetic energy equal to the difference between the core level and the outer-shell states, leaving a doubly ionized atom. Auger electrons that escape without energy loss originate only in the outer 1 to 3 nm of the sample surface, making the technique of Auger electron spectroscopy (AES) very surface sensitive. The primary electron beam may be rastered over an area or focused to a point, allowing data to be collected either from areas as large as 1 mm^2 or points as small as 40 nm in diameter, thus making it possible to map the distribution of an element over the surface in two dimensions. The intensity of a peak is proportional to the amount of the element present, allowing determination of atomic concentrations when appropriate sensitivity factors are used.



The Auger process is a technique for studying surface composition.

Applications

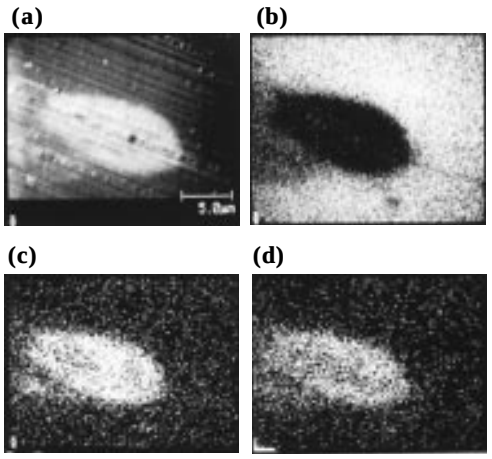
AES is used to identify surface constituents and to determine the composition of the topmost atomic layers. The AES spectrometer may be used as a scanning electron microscope to locate areas of interest followed by a more thorough chemical characterization using AES. The ability to analyze small features with speed and high sensitivity makes AES a powerful technique for problem solving. Area, point, and multipoint analyses are all possible when several features within the imaged area are of interest. Auger line scans across a sample surface can provide a relative concentration of a specific element along a line. Auger imaging or elemental mapping can show the surface distribution of an element. Depth profiling, when coupled with AES, can identify subsurface features. Profiles can be plotted as atomic concentration versus depth, adding a third dimension to the Auger technique. Samples may be fractured in ultra-high vacuum at room temperature or near-liquid-nitrogen temperature to reduce atmospheric contamination. Vacuum sample heating during analysis can be done to track migration of elements across grain boundaries with a hot stage. Corrosion and grain boundary segregation, interface studies, and materials bonding applications are only a few areas where AES can be invaluable.

AES was used to study the magnetic media of a hard disk that had experienced a crash of the read/write head. A discolored

area was seen where the head crash occurred. Identification and distribution of the materials in this area provided clues to the cause of failure. A secondary electron micrograph showed light and dark areas of contrast. We produced AES maps of the carbon, fluorine, and cobalt distribution, and Auger analysis revealed carbon in the dark areas and cobalt, nickel, oxygen, and fluorine in the light areas. The AES maps clearly show that the disk head crash had penetrated the lube layer and protective graphite layer of the CoNi magnetic media. The AES data also suggest the presence of an inorganic fluoride rather than a fluorocarbon, because the fluorine and carbon maps are different. In the area of the head crash, small areas of the CoNi magnetic media were exposed. The stain is actually a refractive effect from small areas of exposed substrate. By penetrating to the magnetic media, the head crash was much more serious than initially believed.

Related Techniques

AES and x-ray photoelectron spectroscopy (XPS) are quite similar in depths probed, elemental analysis capabilities, and absolute sensitivities. While AES has the advantage of higher spatial resolution (tenths of nanometers rather than micrometers), XPS can provide information about the chemical state of an element. Secondary ion mass spectroscopy (SIMS) can be performed with the same instrument as AES and is suited to detection of trace elements as well as hydrogen, which neither AES nor XPS can do.



AES reveals that a head crash has penetrated the magnetic media of a hard disk: (a) secondary electron micrograph showing areas of light and dark contrast, (b) carbon map, (c) fluorine map, and (d) cobalt map.

Sample Requirements & Analysis Time

The samples must be stable under ultra-high vacuum conditions (10^{-8} to 10^{-10} Torr) and under ion and electron beams. Additionally, they must be electrically conductive. Samples cannot be in powdered form. The maximum sample size is 50 mm long by 15 mm wide, or 25 mm in diameter. Maximum thickness is 1.3 mm. With some difficulty, however, it is possible to analyze larger samples. There is no minimum size—if we can see it, we can analyze it. Analysis time ranges from 1 to 24 hours, depending on the application.

Instrumentation

The Perkin-Elmer 600 Multiprobe, equipped with AES and SIMS analyzers, is a surface system with the following capabilities:

- A 0.5- to 25-kV electron gun with minimum beam diameter of 30 nm.
- Duoplasmatron ion gun for in situ sample cleaning or depth profiling at rates of up to 200 nm/min, spot size to 1 mm^2.
- Argon, oxygen, nitrogen, and xenon sputtering gases available.
- Heating stage up to 500°C.
- Ultra-high vacuum fracture of samples at room or near-liquid-nitrogen temperature.
- Quadrupole mass spectrometer for SIMS and electron-stimulated desorption.
- Low-energy electron flood gun for neutralizing insulating SIMS samples.

In addition, we have a transfer vessel that allows us to move a sample between this instrument and an x-ray photoelectron spectrometer under vacuum or argon for extensive analysis by multiple techniques without exposure to air.

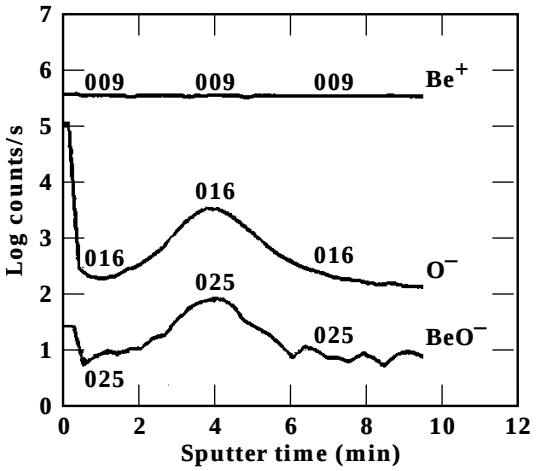
Secondary Ion Mass Spectroscopy

- **Surface sensitive (0.5- to 5-nm analysis depth)**
- **Depth profiling**
- **Qualitative detection of trace quantities of elements**
- **Area scans and two-dimensional maps of elemental distribution**
- **Argon, oxygen, nitrogen, and xenon sputtering gases available**
- **Spatial resolution to 20 μm**

The sample typically is probed with a 4-kV primary ion beam of argon, oxygen, nitrogen, or xenon, causing atoms and molecular fragments to be sputtered from the surface as both ions and neutrals. The ionized species are analyzed in a quadrupole mass analyzer. Results can be given as counts versus mass/charge ratio (in which case all species from 1 to 200 amu may be displayed), or as a depth profile of species of particular interest. Sensitivity varies by many orders of magnitude depending on analysis conditions, the element of interest, and the matrix, making secondary ion mass spectroscopy (SIMS) a strictly qualitative technique.

Applications

To find the Auger electron spectroscopy (AES) detection limit for oxygen and establish the sputter rate of beryllium, we used SIMS to determine the depth profile of a piece of beryllium with oxygen implanted at a depth of 3000 Å below the surface and with a peak concentration of 1193 atomic parts per million. A SIMS profile was taken, using nitrogen as the primary ion beam, and monitoring the O^- (16 amu), BeO^- (25 amu), and Be^+ (9 amu) mass spectrometer signals. The profile was suspended at several points to take AES data of the background and peak signals. It was possible to detect the oxygen signal by AES at the implant peak.



A SIMS profile is used to determine the AES detection limit for oxygen and the sputter rate of beryllium.

Related Techniques

AES can be performed with the same instrumentation and provides higher spatial resolution as well as semiquantitative elemental analysis. X-ray photoelectron spectroscopy can provide information about the chemical state of an element.

Sample Requirements & Analysis Time

Requirements and time for SIMS are the same as for AES. The samples must be stable under ultra-high vacuum conditions (10^{-8} to 10^{-10} Torr) and under ion and

electron beams. Additionally, they must be electrically conductive. Samples cannot be in powdered form. The maximum sample size is 50 mm long by 15 mm wide, or 25 mm in diameter. Maximum thickness is 1.3 mm. With some difficulty, however, it is possible to analyze larger samples. There is no minimum size—if we can see it, we can analyze it. Analysis time ranges from 1 to 24 hours, depending on the application.

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A Perkin-Elmer 600 Multiprobe, equipped with AES and SIMS analyzers, which is a surface system with the following capabilities:

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- Duoplasmatron ion gun for in situ sample cleaning or depth profiling at rates of up to 200 nm/min, spot size to 1 mm^2.
- Argon, oxygen, nitrogen, and xenon sputtering gases available.
- Heating stage up to 500°C.
- Ultra-high vacuum fracture of samples at room or near-liquid-nitrogen temperature.
- Quadrupole mass spectrometer.
- Low-energy electron flood gun for neutralizing insulating samples.

X-Ray Photoelectron Spectroscopy

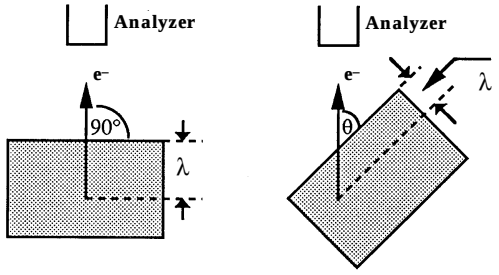
- **Surface sensitive (0.5- to 5-nm analysis depth)**
- **Depth profiling**
- **Semiquantitative detection of all elements except hydrogen and helium**
- **Chemical state identification**
- **Analysis areas of 0.2 or 0.6 mm diameter, 1 mm^2, or 3×10 mm**

The sample is irradiated with either magnesium alpha (1253.6-eV) or aluminum alpha (1486.6-eV) x rays, and the emitted photoelectrons are analyzed. Although the x rays penetrate several micrometers into the sample, the photoelectrons that escape without energy loss originate only in the outer 1 to 5 nm of the surface, making x-ray photoelectron spectroscopy (XPS) a very surface-sensitive technique. By tilting the sample with respect to the analyzer, analysis depth can be varied. A selective lens allows different-sized areas (0.2 or 0.6 mm diameter, 1 mm^2, or 3×10 mm) to be analyzed. Typically, depth profiles can be obtained by simultaneously sputtering with 4-kV Ar^+ ions and acquiring data. All elements except hydrogen and helium can be detected. Because the intensity of a peak is proportional to the amount of the element present, atomic concentrations can be determined using appropriate relative sensitivity factors. Peaks may also shift, depending on the bonding environment of the element, so that it is usually possible to identify the chemical state.

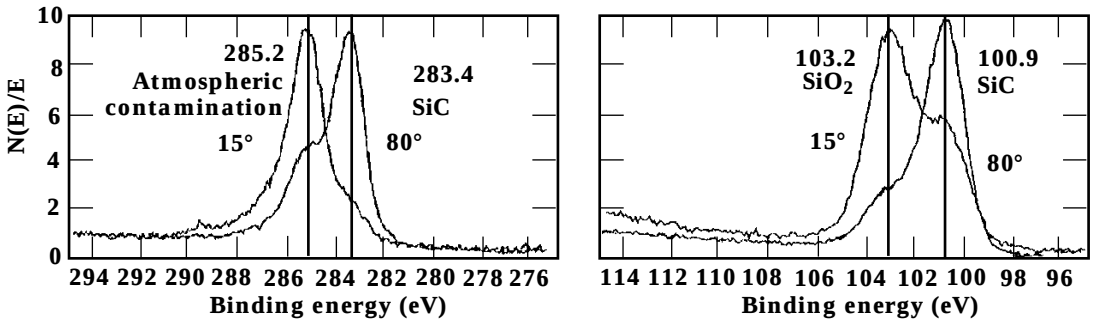
Applications

Electron spectroscopy for chemical analysis (ESCA), or specifically XPS, is the only analytical tool that provides elemental information about composition and chemical-bonding states occurring within the first few atomic layers of most solids. Surface chemistry product performance is important to materials research, product development, and quality control. Widespread applications of ESCA have been in the areas of failure analysis, surface contamination, corrosion of metals, surface oxidation, surface reactions relating to industrial processes, organic/polymer surface analysis, semiconductor materials, optical materials, metallurgical and insulator samples, and thin-film coatings. Elemental identification, atomic composition, and species identification can also be obtained. Modified sample surfaces can be analyzed nondestructively by using the variable angle technique. As the angle is changed, information about the distribution of functional groups can be obtained as well as the depth of the modification. Depth profiling can be used to track impurities across an interface or through a multilayered sample. After surface contaminants are identified, argon ion sputtering can be used to clean the sample surface. Analysis is then repeated to determine the bulk concentration of that sample.

XPS was used to determine if SiC was



The inelastic mean free path of the photoelectron is λ. As the sample is tilted with respect to the analyzer, the effective analysis depth is λ sin θ.



The XPS spectra of carbon 1s (left) and silicon 2p (right).

deposited on a wafer by laser ablation. Scans of the silicon and carbon peaks were taken at analysis angles of 15° and 80° to provide nondestructive depth information of the chemical states present. The XPS spectra of carbon 1s above shows the carbon peak using a take-off angle of 15° for enhanced surface sensitivity. The peak consists almost entirely of atmospheric contamination, with only a small shoulder at 283.4 eV, indicating the presence of carbon as a carbide. Deeper in the sample at an analysis angle of 80°, the carbide peak is revealed as much larger than the surface contamination peak. Similarly, the XPS spectra of silicon 2p shows the silicon peak at 15°, where a large surface-oxidized silicon peak at 103.2 eV is present and the smaller peak of silicon as SiC is visible at 100.9 eV. At 80°, the carbide silicon peak is much larger than that caused by surface oxide.

Related Techniques

Secondary ion mass spectroscopy is suited to detecting trace elements because its higher absolute sensitivity can detect hydrogen and helium; however, this technique removes material. Auger electron spectroscopy provides higher spatial resolution and good depth resolution, but its electron beam sometimes damages the surface. Rutherford backscattering enables nondestructive depth profiling and produces good quantitative results. Because XPS is least destructive to the surface, it is the more broadly applicable surface chemical-analysis technique.

Sample Requirements & Analysis Time

The samples must be ultra-high-vacuum compatible (10^{-8} to 10^{-10} Torr) and stable under x rays and electron beams. Samples can be both insulating and in powdered form. The maximum sample size is 50 mm long if <19 mm wide or 25 mm in diameter. Maximum thickness is 13 mm (larger samples are difficult). There is no minimum size—if we can see it, we can analyze it. Analysis time ranges from 1 to 24 hours, depending on the application.

Instrumentation

The Perkin-Elmer 5400 ESCA system is a small-spot XPS-only system with the following features:

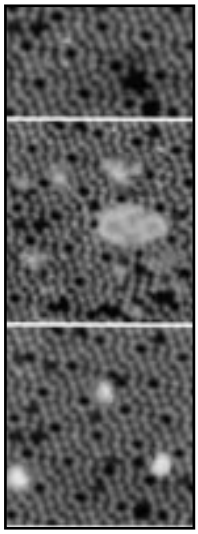
- Analysis areas of 0.2 or 0.6 mm diameter, 1 mm^2, or 3×10 mm.
- Dual magnesium/aluminum anode.
- Ion gun for sample cleaning or depth profiling with argon at rates up to 10 nm/min.
- Tilting stage for angle-resolved XPS.

Scanning Tunneling Microscopy & Atomic Force Microscopy

- **Imaging of surfaces (insulators and conductors) with atomic resolution**
- **Morphology of particles (10 nm to 5 µm)**
- **Measurement of local surface properties (magnetization, electrical charge, density of electronic states, elastic properties, and hardness)**
- **Sample modification (e.g., cutting) on the nanometer scale**
- **Operation in air, vacuum, or fluids**
- **Unrestricted object size—instruments are portable**

Scanning tunneling microscopy (STM) uses an atomically sharp tip attached to a piezoelectric crystal to scan the sample surface. The probe "senses" the proximity of the surface, and a feedback mechanism guides it to stay in constant proximity to the surface when scanning. In STM, the sensing occurs when a bias is applied between the sample and the probe tip, and quantum mechanical tunneling takes place across the gap. A single atom on the probe tip will image the single nearest atom on the sample surface. Because the piezoelectric crystal can be controlled with atomic precision in x, y, and z, STM provides images of individual atoms on a surface. Local electronic structure can be determined by monitoring the dependence of the tunneling current on the voltage applied across the gap. Local chemistry can be induced by increasing the electric field and current density in the gap. STM is restricted to the analysis of electrically conducting surfaces.

In atomic force microscopy (AFM), the probe tip is mounted at the end of a microcantilever, and sensing occurs when forces between the atoms on the tip and those on the sample cause deflection of the microcantilever. Several atoms on an AFM tip will interact with several atoms on the surface, giving a lateral resolution of about 1 nm. Once local morphology is measured, local properties (e.g., magnetization or electrical charge) are determined by monitoring the deflection of the cantilever caused by local magnetic or electric fields as the cantilever is guided over the surface at a known height. Local elasticity or local hardness is determined by measuring the response of the surface to a known force exerted by the probe tip.

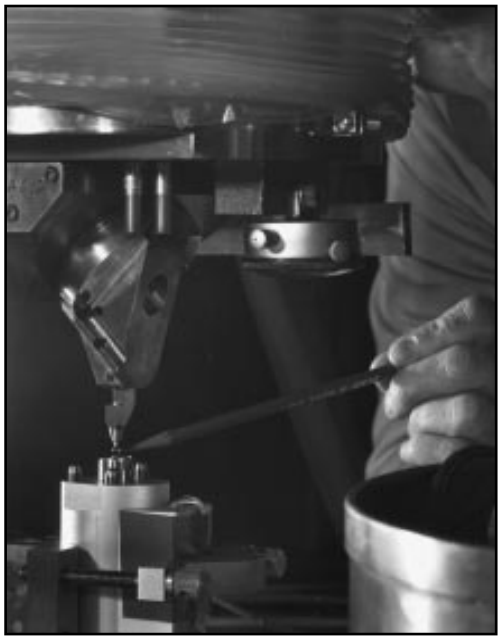


A ultra-high vacuum STM image of C_{60} ("buckyball") clusters deposited on the reconstructed Si 111 (7×7) annealed at various temperatures. The buckyball opens up at ~600 K and reacts with silicon to form SiC.

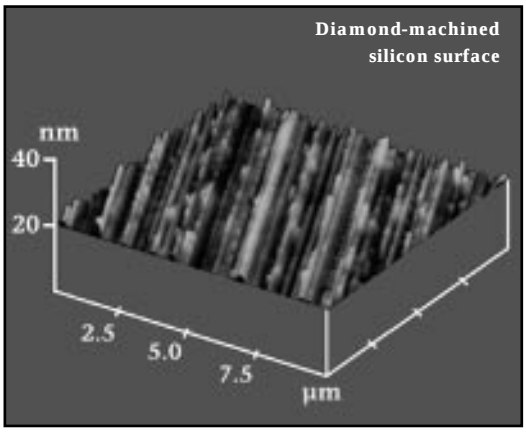
Applications

STM and AFM are powerful techniques that can be used to determine surface morphology of objects of any size of interest, such as laser-fusion implosion spheres, diamond-machined surfaces, and diffraction gratings. STM can be used to investigate the epitaxy of atoms and molecules on surfaces. Because there is little restriction in the type of sample, and operation under vacuum is not necessary, images can provide morphology and volume information of inorganic, organic,

and biological particles. Experiments can be performed to investigate in situ changes in surface morphologies induced by environment, such as corrosion, precipitation, combustion, laser damage, crystal growth, and sputter damage. These instruments can also be used to change surfaces on the nanometer scale, such as to indent, erode, and chemically react surfaces, as well as to determine local electrical, magnetic, and mechanical properties. Demonstrating the range of problems that STM and AFM can address, the figures show chemical reaction experiments done with atomic resolution under controlled conditions in ultra-high vacuum and surface analyses of machined silicon with the stand-alone AFM in situ on the diamond-turning lathe.



Stand-alone AFM analyzing a diamond-turning lathe tool in situ.



Formation of grooves shows conversion of originally smooth cutting tool into a "comb," and "spherical blobs" along machining direction indicates melting of silicon.

Related Techniques

Stylus profilometry provides surface height profiles along a line with atomic resolution in height but indeterminate resolution in x and y. Scanning electron microscopy can image surface features but is restricted in sample size and conductivity requirements and requires vacuum operation. Additionally, it is difficult to get surface morphology at the nanometer level in scanning electron microscopy because of beam-induced contamination.

Sample Requirements & Analysis Time

Samples can be of any form or size—electrically conducting or nonconducting and tenths of nanometers in dimension to massive because there is no size limit. Samples 0.1 nm to 150 mm in size are analyzed on sample holders fitted to the instruments. Samples larger than 10 mm are analyzed by fitting the scanning probe onto the surface of the sample. The instrumentation is portable, so in situ measurements are possible.

Sample preparation time is minimal and a surface scan takes minutes. Consequently, routine analysis of surface morphology is quick. More detailed experiments require more time.

Instrumentation

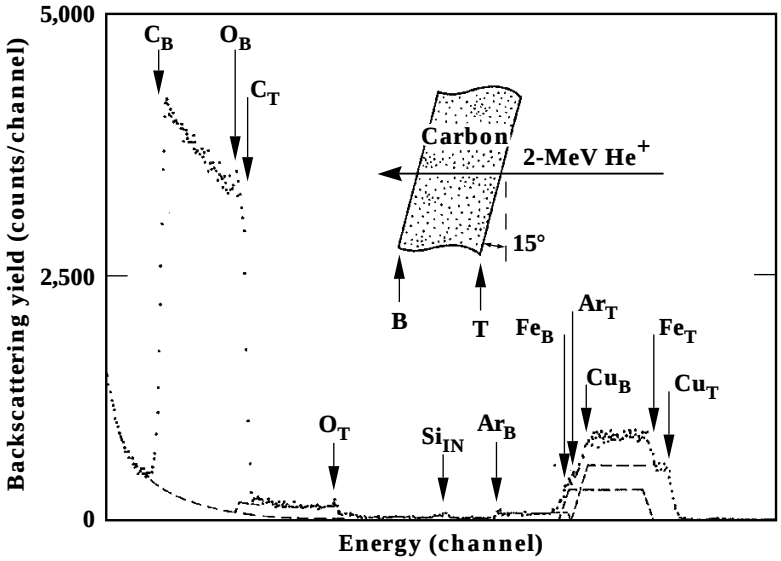
- Digital Instruments Nanoscope II and Nanoscope III with many attachments, operating in air or fluid.
- Digital Instruments Large Stage AFM/STM capable of accepting samples up to 150 mm in diameter.
- Digital Instruments stand-alone AFM/STM (for in situ analysis of large objects).
- McAllister STM for operation in ultra-high vacuum.
- Park Scientific AFM/STM for operation in ultra-high vacuum.
- Nano-indentor.

Data readouts include digital record of z as function of x and y, displayed in false-color images; Fourier analysis of surface morphology; surface roughness analysis; section analysis along any line on the surface; elasticity as function of x and y; and hardness at x and y.

MeV Ion-Beam Characterization of Materials

- **Surface and near-surface sensitivity (0- to 10-μm analysis depth)**
- **Quantitative analysis of all elements**
- **Elemental depth profiles**
- **Nondestructive methods**

Ions with energies of about 0.4 to 8 MeV can provide quantitative, nondestructive elemental analysis of the top 0 to 10 μm of materials, using one or more of four ion-beam techniques. Rutherford backscattering (RBS) depends upon the energy of ions elastically scattered back from atomic nuclei in the sample. Particle-induced x-ray emission (PIXE) involves the production of characteristic x rays from inelastic scattering of ions with inner-shell electrons in the material. Nuclear reaction analysis (NRA) consists of energy spectrometry of nuclear reaction products produced by the incident ions. Forward recoil spectroscopy (FRS) determines the energy of the lighter atoms recoiled out of the material by collisions with heavier incident ions.



Helium ion backscattering spectrum for free-standing carbon foil. Subscripts "T" and "B" refer to the energy position for helium scattered from the indicated element at the top or base of the foil, respectively.

Rutherford Backscattering

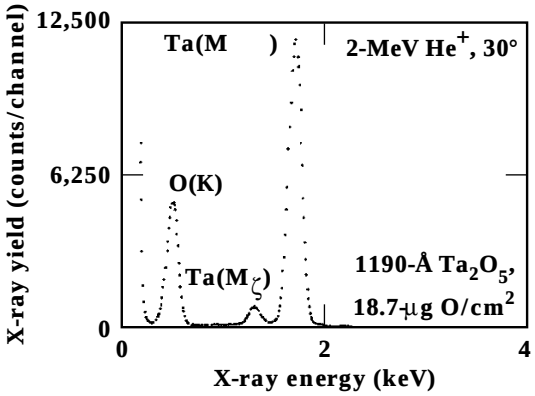
In ion backscattering spectrometry, the energy of ions elastically scattered back from nuclei in the sample is measured. Simple Coulombic or RBS using helium ions and protons has proven to be most generally useful. Resonant and nonresonant elastic nuclear scatterings have interaction cross sections for low-atomic-number target atoms that are more than ten times those for RBS, and can provide unique insights into the composition and properties of some specimens. In all cases, the energy of a backscattered ion depends upon two processes: the loss of energy from the transfer of momentum to the target atom during the backscattering collision and loss of energy with depth through the target both before and after scattering from slowing by small inelastic scattering with electrons of the material. Thus, interpretation of backscattering spectra yields information about both the mass and depth distribution of specimen elements with a depth resolution of about 30 nm.

The first figure shows the 168° backscattering spectrum from a free-standing carbon foil. The spectrum clearly shows that contamination by oxygen (1.6 at.%), argon (0.19 at.%), iron (0.48 at.%), and copper (0.59 at.%) exists uniformly throughout the entire foil thickness.

Particle-Induced X-Ray Emission

PIXE is a quantitative, nondestructive analysis technique that provides spectra of characteristic x rays emitted when high-energy particles ionize atoms of a specimen. Because bremsstrahlung background in the x-ray spectrum produced by ion excitation is greatly reduced compared to that produced by electron excitation, the detection limits using PIXE are between 10 and 10,000 times better than those using electron excitation. PIXE can be used for elements with atomic numbers greater than five.

PIXE and RBS are well matched as complementary techniques because, for a given ion energy, the x-ray production cross section (σ_x) decreases as a high power of the atomic number of target atoms, whereas the Rutherford cross section increases as the square of the atomic number. In addition, PIXE provides a clear distinction between atoms with similar atomic numbers, while



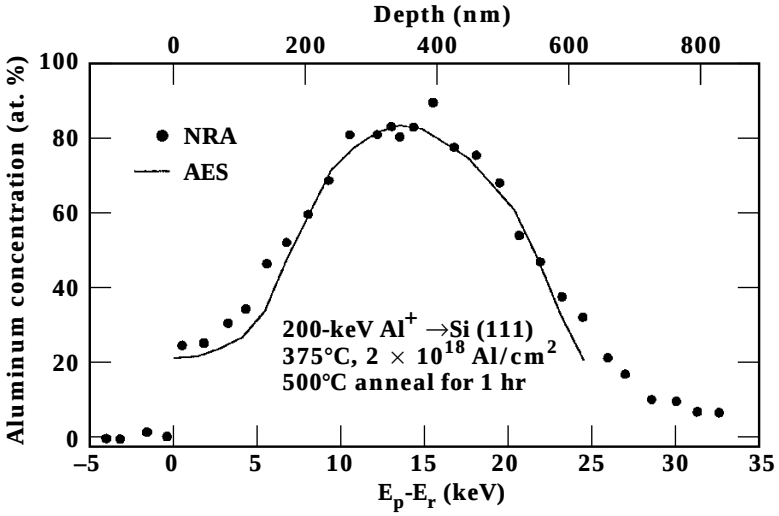
Helium-ion induced x-ray spectrum for an anodized tantalum specimen.

RBS does not always yield an unambiguous identification for atoms with high atomic numbers. However, the depth resolution for profiling for RBS is much better than that for PIXE. Finally, spectra from both techniques can be acquired simultaneously.

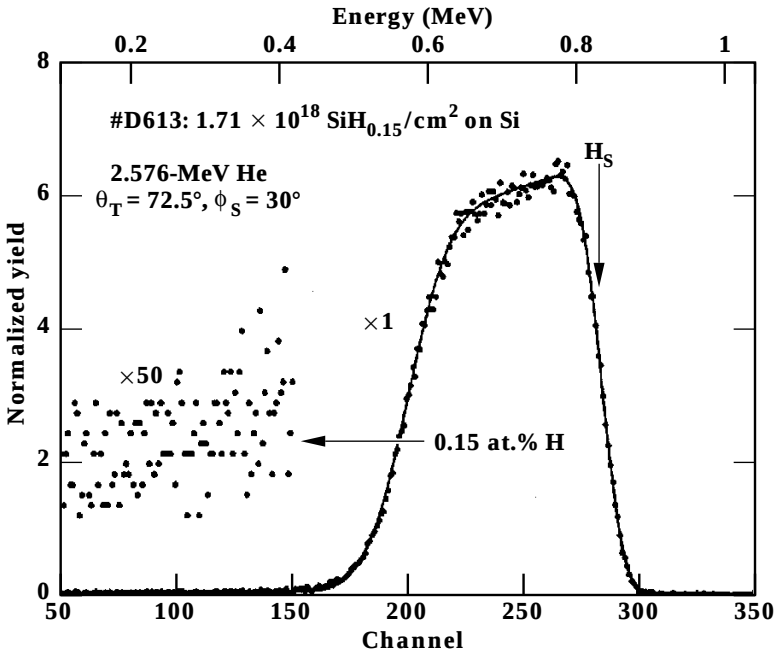
Nuclear Reaction Analysis

Ion-induced nuclear reactions often result in the prompt emission of reaction products such as protons, alpha particles, and gamma rays that are uniquely related to the nuclei of the incident ions and the target atoms. Because the reactions are isotope-specific, the background signals tend to be very low, making NRA ideal for isotopic tracer experiments. In contrast to RBS, there is no simple analytical expression for the cross sections, and standards must be used to analyze the materials. For ion energies less than 8 MeV, NRA has been applied to elements with atomic numbers between 1 and 15.

The reaction cross sections of many ion-induced nuclear reactions have sharp resonances as a function of ion energy. These resonances can be used to do depth profiling by varying the incident ion energy. For example, the figure on depth distribution of aluminum implanted into silicon shows the depth distribution of aluminum obtained by NRA using the p-gamma resonance reaction for a proton energy of 992 keV (i.e., E_r) compared to that obtained by Auger electron spectroscopy. The concentration scale for the Auger electron spectroscopy profile was established by normalizing the peak aluminum concentration to the value found for the peak NRA concentration.



Depth distribution of aluminum implanted into silicon as determined by NRA and Auger electron spectroscopy.



FRS for an amorphous silicon–hydrogen layer on silicon.

Forward Recoil Spectroscopy

When the mass of the incident particle is equal to or greater than the mass of the target atom, elastic backscattering cannot occur. However, a large part of the incident ion energy can be transferred to the lighter target atom, which then recoils into a forward angle. In FRS, energy spectroscopy of these elastically recoiled atoms yields the initial depth distributions of the recoiled atoms. Generally, the incident ion and detected recoiled atom have paths at small angles (<30°) with the surface of thick specimens. Thin, free-standing foils are an exception, because the recoiled atoms can escape through the foil to a detector. FRS allows all elements to be analyzed with a depth resolution of about 30 nm and at much higher cross sections than those for NRA. Thus, FRS is very useful for surface and bulk analysis of isotopes of hydrogen and other light elements when depth resolution is not critical.

Ion Channeling

A combination of one of these analysis techniques together with channeling of ions through the open directions (axial or planar channels) of monocrystalline materials can be used to determine the location of impurity atoms in either interstitial or substitution sites and to assess lattice imperfections (i.e, damage) in the near-surface region.

Related Techniques

In contrast to other surface analysis techniques such as Auger electron spectroscopy, x-ray photoelectron spectroscopy, and secondary ion mass spectroscopy, ion-beam techniques require no specimen preparation and are nondestructive; that is, essentially no material is consumed during analysis. The ion-beam analyses are quantitative because the cross sections for interactions of the ions with atoms in the material are either well known or can be determined using known standards. In addition, initial analysis with MeV ions can often provide considerable information and may suggest additional techniques to answer questions raised but not answered by the ion-beam techniques.

Sample Requirements & Analysis Time

In general, samples must be nonvolatile solids because the sample is usually analyzed in a vacuum of $<10^{-6}$ Torr. In addition, monocrystalline or nearly monocrystalline samples are required for channeling. Typically, the ion beam probes a lateral region of a few square millimeters; thus, sample dimensions are normally 5 to 50 mm, but smaller and larger specimens can be accommodated.

RBS, PIXE, and FRS measurements each take typically about 1/2 hour per specimen, but the data can be taken simultaneously. Quantitative analysis of the data usually requires about 2 hours per spectrum. The NRA measurements involve sequentially increasing the ion energy to increase the probing depth and require 4 to 8 hours per specimen, with quantitative analysis taking an additional 2 to 4 hours per specimen. Combining channeling with one of the above techniques increases the measurement and analysis time by factors of 2 to 4.

Instrumentation

The ion accelerator is a National Electrostatics Corporation Model 4UH, which is a single-ended pelletron with a maximum terminal potential of 4 MV. The cryopumped analysis chamber houses the detectors and a large, five-axis Klinger stage that can accept specimens as large as 7 in. in diameter by 1 in. thick. For RBS and FRS measurements, standard surface barrier detectors are used for the ion spectroscopy. An ultra-thin-windowed Si(Li) detector is used for the PIXE analysis. A 3-in. NaI detector is used for gamma spectroscopy during NRA.

Comparison of MeV ion-beam techniques for characterizing materials.

Detection capability	RBS	PIXE	FRS	NRA
Elements detectable (in principle)	$Z > 1$	$Z \geq 3$	$Z \geq 1$	$Z \geq 1$
Elements usually detected	$Z \geq 3$	$Z \geq 6$	$9 \geq Z \geq 1$	$15 \geq Z \geq 1$
Elements detected simultaneously	Many	Many	Few	One
Elemental specificity	Good	Very good	Good	Very good
Quantitative nature (with or without standards	Without	With & without	With & without	With
Accuracy:				
Concentration	1–3%	<2–10%	1–3%	3–5%
Layer thickness	3–10%	3–10%	3–10%	3–10%
Maximum sensitivity:				
Surface (ML)	0.001–100	0.01–5	0.01–0.1	1–10
Bulk (at.%)	0.001–10	0.0001–10	0.01–1	0.0001–10
Maximum depth probed (mm)	~5	~5	~2	~5
Best depth resolution (nm)	~3	100	~100	<10

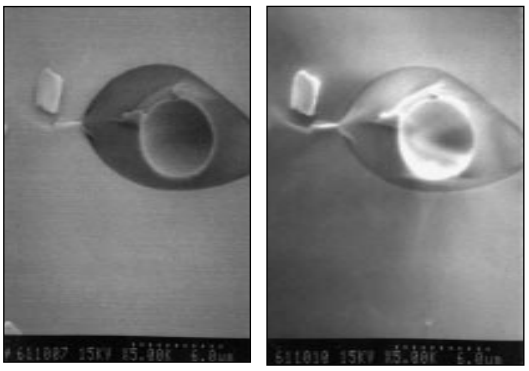
Scanning Electron Microscopy

- **Imaging of surface topography (20× to 500,000× magnification, 1.5-nm resolution, and large depth-of-focus)**
- **Imaging of different chemical phases**
- **Identification of all elements heavier than beryllium**
- **Semiquantitation of concentration of all elements heavier than neon**
- **Three-dimensional imaging (stereo)**
- **Particle analysis and image processing (size, shape, and distribution)**

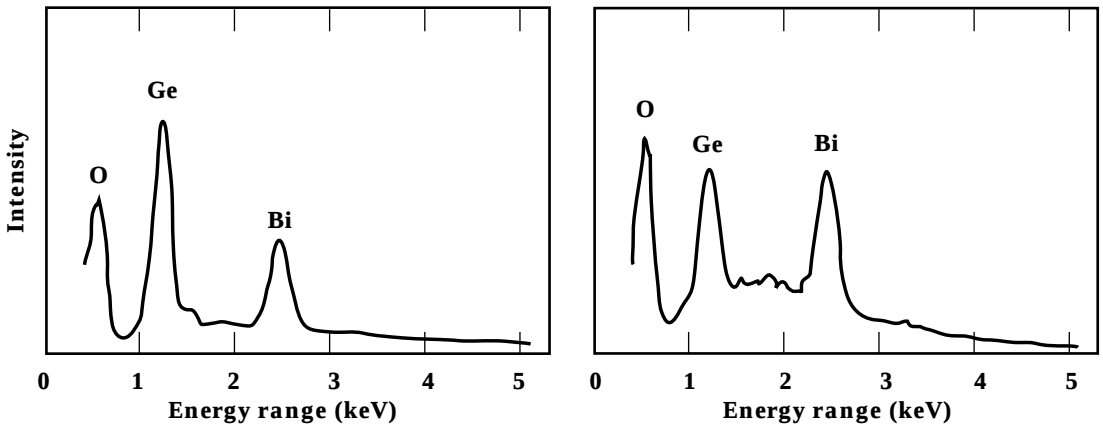
An electron beam interacts with the sample surface, causing emission of secondary electrons, backscattered electrons, and characteristic x rays from depths of up to 50 nm, 500 nm, and 1 mm, respectively. The secondary electron signal is used to produce an image whose contrast depends on topography and composition. Because the intensity of the backscattered electron signal depends on the average atomic mass, scanning electron microscopy (SEM) is used to image compositional differences. The characteristic x-ray energies produced by the sample surface are analyzed by energy dispersive spectroscopy (EDS) to identify, semiquantify, and map elemental constituents of the imaged surface.

Applications

SEM is a powerful adjunct to the light microscope for viewing surface topography obscured by limited depth of focus and resolution. Rough and irregular surfaces can be observed easily with secondary electron imaging. Observations of fractography features for determining tensile strength, fatigue, and toughness characteristics of metals, ceramics, and composite materials are a few applications of SEM. Using the backscattered imaging mode, SEM also can differentiate chemical phases such as precipitates, inclusions, and interfaces of materials. Combining stereo imaging with secondary backscattered electron imaging can resolve spatial relationships of surface features that are not obvious in two-dimensional imaging. Particle analysis of size, shape, and distribution can be done using SEM with image processing. With the addition of an energy dispersive x-ray system, EDS can be performed on imaged surfaces for chemical analysis. Elemental identification and semiquantification of bulk concentrations can also be obtained. Elemental identifications down to boron and semiquantification of elements down to sodium with sensitivities of 0.1 wt% are possible.



The SEM micrographs are images of an inclusion within a crystal of $BiGe_{12}O_{20}$. The inclusion consists of a topographically raised mound with a central pit, as shown in the secondary electron image (left). The backscattered image (right) reveals the atomic contrast between matrix and inclusion.



EDS analysis shows that the inclusion pictured in the micrographs is enriched in germanium (left) relative to the matrix (right).

Related Techniques

The electron microprobe, based on the same principle as SEM, is optimized to identify and quantify elemental abundance in samples by using x-ray wavelength dispersive spectroscopy. In general, SEM uses x-ray EDS to analyze elemental concentrations in a sample. The SEM, with its smaller electron-beam spot size and current, is optimized for high-resolution imaging. However, the electron microprobe, with its wavelength spectrometers, provides more precise quantitation of elemental concentrations.

Sample Requirements & Analysis Time

Solid, nonvolatile electron-beam-stable samples of submicrometer to 25 mm in diameter are suitable for full visual translation. Samples can be as large as 40 mm high by 75 to 100 mm in diameter, but the region of interest must be contained in the 25-mm translation limits of the sample stage that is central to the electron beam. Larger than normal samples may limit backscatter imaging and x-ray analysis. Samples are usually examined in an as-submitted states. However, a conductive coating (usually gold or carbon) can be used to prevent the effects associated with sample charging.

Some samples can be analyzed in a few minutes. However, several hours may be needed if extensive preparation or chemical analysis is required.

Instrumentation

Two Hitachi (models S-800 and S-4500) field-emission scanning electron microscopes are available. The S-800 is capable of magnifications of 20× to 300,000× with resolutions down to 2 nm. The new S-4500 is capable of magnifications of 20× to 500,000× with resolutions down to 1.5 nm. Both have low-voltage imaging capabilities for low sample and charging effects and some image-processing capabilities. The S-4500 has greater digital imaging capabilities and an additional secondary electron detector in the objective lens. This detector improves image contrast and resolution on low-voltage samples. Both instruments have energy dispersive x-ray systems.

Electron Microprobe Analysis

- **Quantitative detection of all elements except hydrogen, helium, and beryllium**
- **Chemical phase determination**
- **1-μm spatial resolution**

Electron microprobe analysis (EMP) uses a focused beam of electrons to generate emission of characteristic x rays and secondary and backscattered electrons. The characteristic x rays are analyzed using wavelength dispersive spectroscopy (WDS) to quantitatively determine the chemical composition of the primary and secondary phases and inclusions with a spatial resolution of about 1 μm. The secondary and backscattered electrons produce images of the topography and elemental variations, respectively. The microprobe is capable of detecting all elements heavier than boron present at levels of 0.1 wt% or more.

Applications

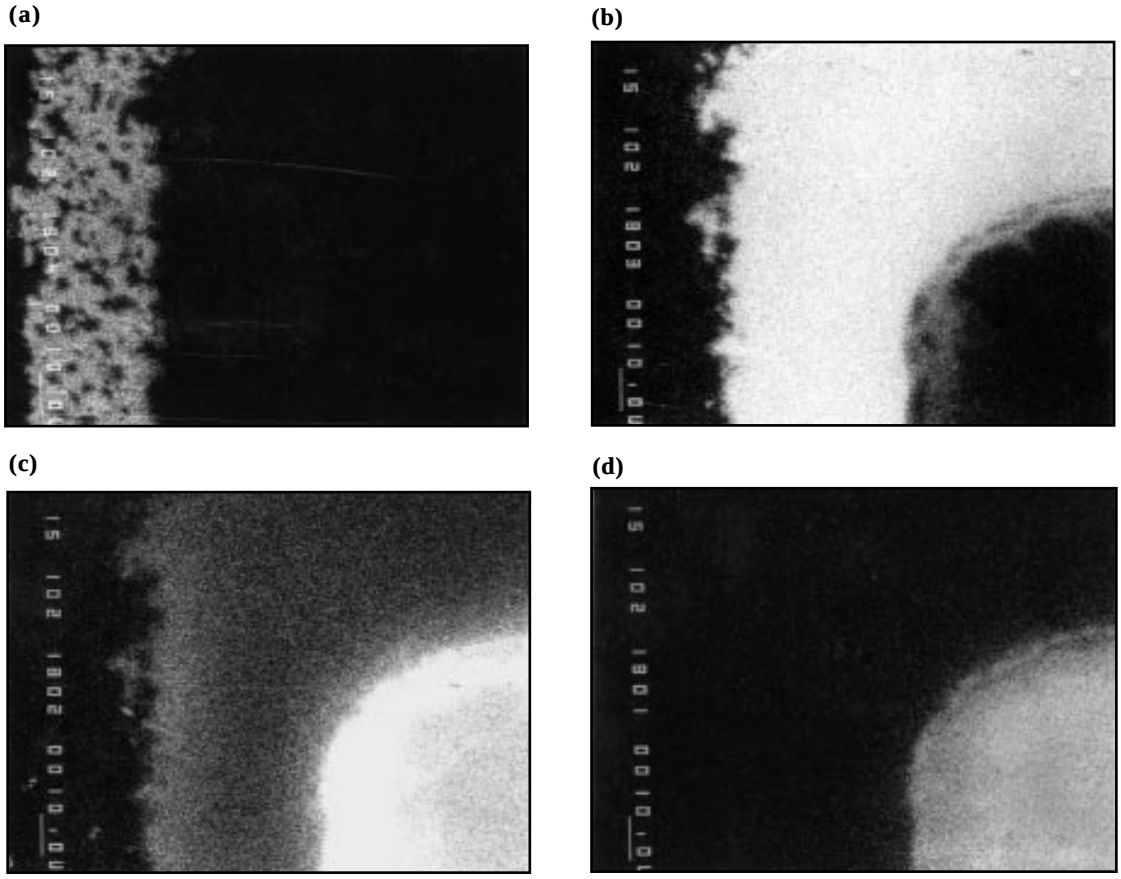
Because EMP provides quantitative information on composition at the micrometer scale, it is ideal for analyzing heterogeneous materials such as ceramics, alloys, composites, and geologic media. The strength of EMP is that it uses x-ray WDS, which has high spectral resolution, thereby eliminating overlap and deconvolution problems. EMP provides a powerful tool for determining unknown compositions by providing complete numerical concentration values of imaged areas.

Such quantitative x-ray mapping is shown here in the EMP analysis of a braze joint of alumina to Kovar (Fe–29Ni–17Co). To obtain a good glass-to-metal seal, the alumina was metallized with a paste mixture of Mo–10Mn–10SiO_2. Nickel was plated onto the paste, and Kovar and the two materials were brazed with copper at 1100°C. The x-ray map shows a fairly homogenous distribution of nickel in the joint, indicative of a good braze. Note also the high concentration of nickel in the Kovar material.

Topographical image of a braze joint of alumina (on the left side) to Kovar (right).

Related Techniques

Scanning electron microscopy (SEM) is based on the same principle as EMP. SEM is optimized to give low beam currents, high spatial resolution, and large depth of field; EMP is optimized to give high beam currents, high spectral resolution, and shallow depth of field. The energy dispersive spectrometer in SEM can provide qualitative chemical analysis, while the WDS spectrometer in EMP is used for quantitative analysis for trace-element determination.



X-ray maps of (a) molybdenum metallization, (b) copper braze, (c) nickel distribution, and (d) iron in Kovar.

Sample Requirements & Analysis Time

Solid samples, either conducting or nonconducting, which are stable in vacuum, can be analyzed with EMP. Sample dimensions cannot exceed a diameter of 20 mm and a thickness of 10 mm. An important requirement is that all samples must be polished to a 1-µm surface finish and cleaned carefully. Insulators require a conductive coating, usually carbon.

Full quantitative analysis requires a careful standardization procedure that takes several hours. Actual sample analysis takes from 1 hour to a half day per sample. Mapping requires longer times.

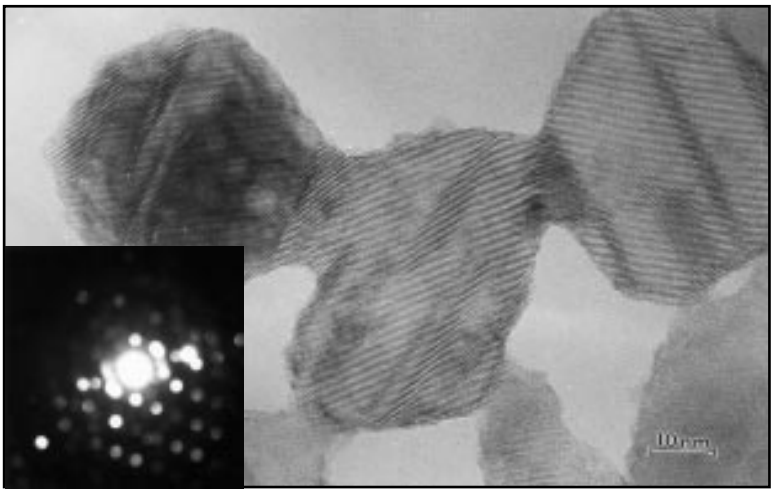
Instrumentation

A JEOL 733 microprobe with three spectrometers and a Kevex energy-dispersive spectrometry detector are available.

Transmission Electron Microscopy

- **General microstructure characterization**
- **High-resolution imaging of atomic sites**
- **Crystal structure determination by electron diffraction**
- **Microchemical analysis of 3-nm^2 areas**

In transmission electron microscopy (TEM), high-energy electrons are focused on, and subsequently transmitted through, a thinned sample. Some electrons are diffracted in known Bragg directions, others lose energy and scatter inelastically, still others produce characteristic x rays from the sample. General magnified images of microstructures are formed using the transmitted and diffracted beams in various configurations. Diffraction effects produced by using only two beams in the microscope result in high-contrast images of grains, dislocations, interfaces, and precipitates. Multiple-beam interactions are used to generate images of atomic periodicity. The sample can be tilted in various orientations to produce characteristic electron diffraction patterns, which give atomic structural information. Qualitative and quantitative chemical analyses are obtained by analyzing x rays dispersed at varying energies or analyzing scattered electrons at characteristic energy-loss states.



High resolution of non-annealed titania–tantala aerogel and related microdiffraction pattern.

Applications

TEM is used for obtaining images of microstructures smaller than approximately 10 nm (for example, dislocations, small precipitates, or atom clusters in metals, ceramics, polymers, or composites). Modern high-resolution transmission electron microscopes are capable of resolutions down to 0.16 nm. Fringes in the image are representative of lattice spacing of the crystal structure. The high-resolution transmission electron microscopes can be used to examine atomic steps on thin, nanolayered, electronic materials or to determine surface planes on catalyst crystallites. The micrograph here shows a high-resolution image of beads in ceramic aerogel material. The sample was found to consist of 5- to 35-nm-sized crystallites displaying random orientation of surface planes. This result was unique because it had been assumed that aerogels generally take on an amorphous structure.

Nontraditional TEM samples also can be imaged. Polymers, suspensions, biological tissue, and emulsions are imaged

using low-voltage, low-dose TEM mode when prepared by surface replication and/or freeze-fracture techniques. Using these sample preparation methods, we have examined the microstructure of organic aerogel samples in solution before solidification.

TEM can be used to investigate in situ the effects of heating, cooling, and other environmental variations on materials—results are monitored by live video hookup to the microscope. In situ heating performed up to 1100°C is excellent for experiments on diffusion and solute segregation.

The probe characteristics of TEM are such that areas as small as 2 nm in diameter can be analyzed for crystal structure information using microdiffraction techniques. Applications include atomic structure characterization, phase determination, epitaxial relationships, specimen thickness, and dislocation analysis. For example, using a 60-nm-sized beam, we obtained a microdiffraction pattern from one aerogel bead (as shown in the micrograph).

Related Techniques

Because TEM requires such rigorous specimen preparation procedures, investigating specimens in the scanning electron microscope or electron microprobe first may be cost-effective, unless the size of microstructures is already known to be smaller than the resolution capability of the scanning electron microscope or if crystallographic information is needed. X-ray diffraction may reveal crystal structure and defect nature on the bulk scale if the sample is large enough and homogeneous. X-ray diffraction is useful as a complementary analysis tool, but does not give data on amorphous materials. Other analytical techniques that use detectors attached to the TEM are energy dispersive spectroscopy and parallel electron energy-loss spectroscopy.

Sample Requirements & Analysis Time

Samples must be 3 mm in diameter with a thickness less than 50 nm. Because of this requirement, sample preparation can be time-intensive. Powders require only a few minutes of sample preparation, and metals can be thinned in about 1 to 4 hours by electropolishing first. Ceramics and geological media may take up to a week to cut, core, polish, dimple, and ion-mill. Cross-sectioned samples can also take up to a week to prepare. Efficiency of sample preparation is dependent upon prior knowledge of preparation variables and the number of samples to prepare.

General microstructural images of the sample require about 8 hours to image, print negatives, and analyze. Diffraction work and chemical analysis take longer, depending upon the amount of information required and the complexity of the structure.

Instrumentation

Available microscopes include

- A JEOL JEM200CX TEMSCAN with Kevex energy-dispersive spectrometer and Gatan electron energy-loss spectrometer for routine analysis.
- A JEOL JEM4000EX for high-resolution imaging.
- A TOPCON EM-002B with Link energy-dispersive spectrometer for high-resolution imaging, microprobe diffraction, and chemical analysis over the same regions.

Specimen preparation equipment includes diamond wheel saws, spark cutters, ultrasonic and slurry corers, microtome systems, grinders, ion mills, jet electropolishers, and surface coaters.

Energy Dispersive Spectroscopy

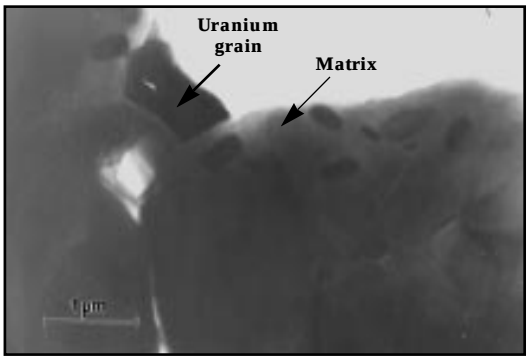
- **Qualitative or quantitative chemical analysis**
- **Line scan or area mapping**
- **Probe size as small as 2 nm**
- **Elemental analysis for elements with atomic numbers greater than six**

In energy dispersive spectroscopy (EDS), a beam of energetic electrons ionizes the sample material, causing an inner-shell electron to be removed. To return to ground state, an electron from the outer shell fills the vacant shell and emits an x ray in the process. The emitted x ray is characteristic for each material because the x-ray energy is equal to the transition energy from the outer shell to the inner shell. The x rays are collected and dispersed over their energy range by a series of signal-processing electronics. Energy of peaks identify the elements, and peak heights provide their relative amounts.

Applications

EDS can detect chemical content with an accuracy of approximately 4 to 5% at a minimum detection limit as low as 0.1 wt%, depending upon the specific sample and operating conditions. When coupled with a transmission electron microscope, microchemical analysis can be performed on microstructures as small as 2 nm. For example, quantitative analysis of precipitates in alloyed materials is possible with EDS. Qualitative analysis of segregants at grain boundaries and defects is yet another application. Line scans can be performed at interfaces of multilayered materials, or area maps generated to show placement of specific elements over an area of interest.

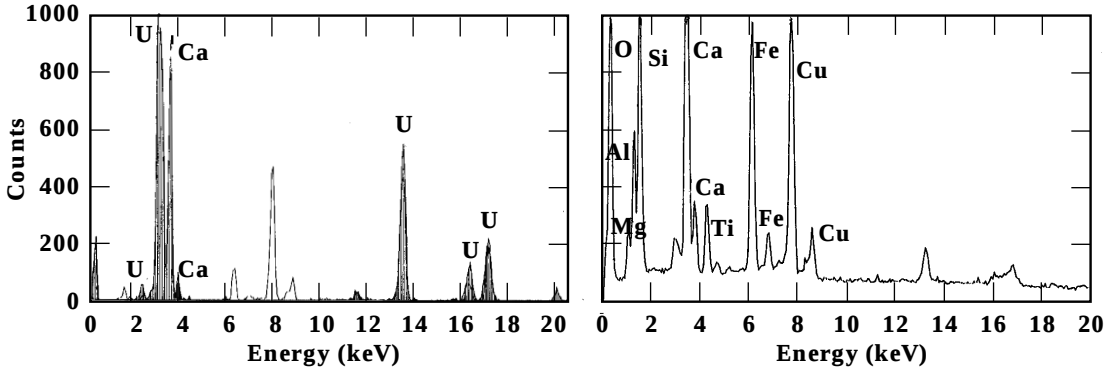
Semiquantitative EDS was performed on fly ash materials containing small amounts of uranium. It was important that the uranium in the material be alloyed with the fly ash constituents as a crystalline phase rather than an oxide or glassy phase. The major uranium-containing phase in one of the fly ash samples was identified as tetragonal $CaUO_4$. The calcium uranate grains in the micrograph shown here appear dark, compared to the lighter matrix of aluminan diopside—$Ca(Mg, Fe, Al)(Si,Al)_2O_6$.



Transmission electron microscopy image of fly ash materials containing uranium.

Related Techniques

EDS can be applied to electron column instruments such as the scanning electron microscope, the transmission electron microscope, and the electron microprobe, making microanalysis easy, rapid, and efficient. EDS has higher spatial resolution than x-ray diffraction, but lower beam current and poorer peak resolution than x-ray wavelength dispersive spectroscopy in electron microprobe analysis.



The EDS spectra of calcium uranium oxide grain (left) and aluminan diopside matrix (right).

Sample Requirements & Analysis Time

Samples need to be vacuum- and electron-beam stable. Sizes of samples depend upon the instrument used: scanning electron microscopy samples can be virtually any size that will fit into the column, while transmission electron microscopy samples are 3 mm in diameter. Scanning electron microscopy samples are usually examined in an as-submitted state. However, a conductive coating (usually gold or carbon) can be used to prevent the effects associated with sample charging. Transmission electron microscopy samples require thicknesses less than 100 nm and are prepared using various techniques. Powders require only a few minutes of sample preparation, and metals can be thinned in about 1 to 4 hours by electropolishing first. Ceramics and geological media may take up to a week to cut, core, polish, dimple, and ion-mill. Cross-sectioned samples of semiconductor material can also take up to a week to prepare.

Microchemical analysis can be achieved in just 2 to 4 hours if qualitative information is required. However, quantitative analysis may take longer, particularly if many areas will be examined and the microstructure is complex.

Instrumentation

Both scanning electron and transmission electron instruments are equipped with Kevex ultra-thin window Si(Li) x-ray detectors capable of detecting boron and all elements heavier than boron. The x-ray detector in the scanning electron microscope is also equipped with a beryllium window for detection of all elements heavier than sodium. The Kevex Microanalysis System 8000 software packages include advanced digital imaging for image analysis, fast x-ray mapping, and semiquantitative and quantitative analysis.

Parallel Electron Energy-Loss Spectroscopy

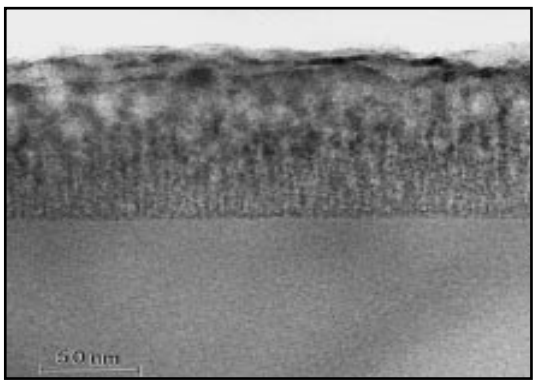
- **Quantitative analysis of elements from beryllium to bromine**
- **Electronic and chemical bonding information**
- **Thickness measurements**
- **Spectral resolution to 10 eV**

In parallel electron energy-loss spectroscopy (PEELS), electrons are transmitted through a sample and scattered inelastically by the electron shells of individual atoms. The transmitted electron loses energy from excitation of the bound electrons of the sample to higher energy states. The energy transfer is recorded by energy-distribution spectra with three distinct regions: the zero energy-loss region is a symmetrical peak that represents electrons with negligible or no energy loss, the low-loss region (1 to 50 eV) represents plasmon interactions or inelastic scattering with the valence electrons in metals, and the rest of the spectrum (50 to 3000 eV) is composed of characteristic edges from inelastic interactions with the deeper core levels of the atom. The detailed shape of the spectral profiles gives information about the electronic structure, chemical bonding, and average nearest neighbor distances.

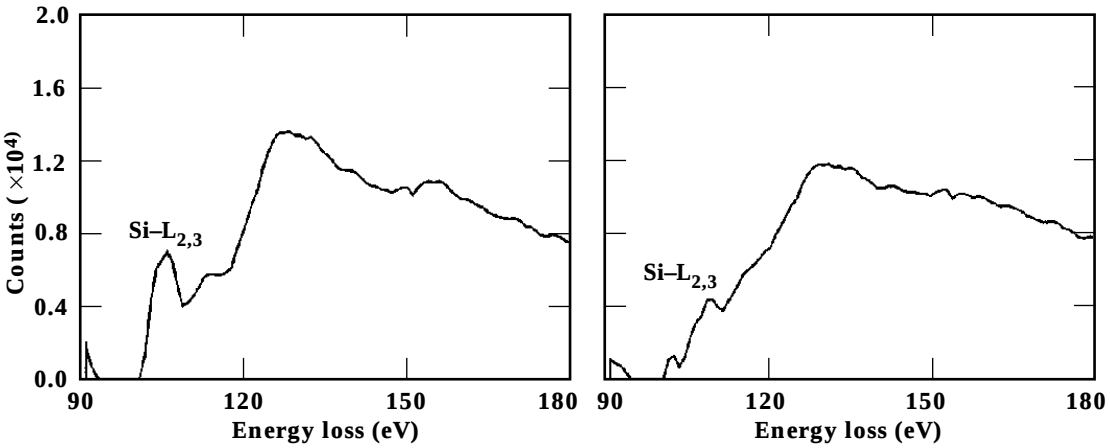
Applications

The characteristic edge peak in the PEELS spectrum can be used to qualitatively and quantitatively identify elemental composition. PEELS is useful particularly for materials with atomic numbers from 3 to 35 because absorption problems are minimized. The edges additionally can determine the chemical bonding state. For example, there are different peak shapes and shifts characteristic of diamond carbon versus graphitic or amorphous carbon. Studies of the plasmon peak can provide information about dielectric properties of the solid or about measurements of valence electron densities leading to peak shifts such as those observed between metals and their hydrides. Examination of near-edge structure determines near-neighbor distances and coordination numbers of atomic species.

PEELS was used to characterize a 50-nm layer of silicon and carbon after laser irradiation to determine whether β-SiC had been synthesized. The micrograph below shows the bottom region of the layer, which consists of small columnar grains that proved to be β-SiC, and the upper polycrystalline region, which was determined to be mixed Si and β-SiC grains. Determination of different phases



Transmission electron micrograph of deposited silicon and carbon on amorphous quartz after 138 mJ of laser irradiation.



The PEELS spectrum of silicon L-edges from the columnar grains revealing the sharp first peak ($L_{2,3}$) that is characteristic of β-SiC (left), and PEELS spectrum of silicon L-edges from the surface region showing the presence of elemental silicon where the $L_{2,3}$ peak is lower and more rounded than the $L_{2,3}$ peak from β-SiC (right).

was made by comparing characteristic peak shapes from an atlas of PEELS spectra with standard peak shapes as well as by energy edges.

Related Techniques

PEELS is analogous to x-ray absorption spectroscopy, particularly extended x-ray absorption fine structure and x-ray absorption near-edge structure. The distinctions between the electron case and the x-ray case are the higher resolution obtained by PEELS because of the smaller wavelength of electrons compared to x rays and the smaller sample area available for analysis because of the focus of the electron optics compared to synchrotron collimation. Signals for PEELS have higher peak-to-background ratios and much more resolvable peaks than spectra from energy dispersive spectroscopy. Because the PEELS detector is attached to a transmission electron microscope, energy dispersive spectroscopy images can be made of a specific area of interest.

Sample Requirements & Analysis Time

Samples are prepared as for the transmission electron microscope, but thickness requirements are more stringent. The area of interest must be no thicker than 60 nm for elements with a low atomic number such as aluminum and 30 nm for higher atomic number materials such as iron and nickel, to avoid multiple scattering events. Specimen preparation is therefore time-consuming and may take several days.

The PEELS analysis requires rigorous calibrations with standards to obtain reliable data; analysis times vary from one day to a week.

Instrumentation

A Gatan PEELS spectrometer with Gatan EL/P software is used with a Macintosh computer. The PEELS spectrometers are available on a JEOL TEMSCAN 200CX transmission electron microscope with probe sizes to about 60 nm diameter and on a Philips 400ST-FEG analytical transmission electron microscope with probe sizes as small as 2 nm in diameter.

X-Ray Diffractometry

- **Semiquantitative analysis of specific compounds and phases**
- **Accurate determination of crystal lattice parameters**
- **Characterization of structural properties**
- **Characterization of thickness of thin films and multilayers**

When a randomly oriented aggregate of small crystal fragments (such as a powder) or a single crystal is irradiated with a monochromatic beam of x rays, the various planes of atoms diffract the x-ray beam at angles determined by spacing between the planes. X-ray diffractometry (XRD) records the diffracted beams as a function of scattering angle on film placed concentrically around the sample or by a scanning counter. Each crystalline phase present in the sample supplies its own unique contribution to the total diffraction pattern. Unknown compounds and phases can be identified by their characteristic patterns. In mixtures, the relative intensities of the patterns can be used to estimate the concentrations of the phases present, and the breadths of the peaks in the pattern are characteristic of the average crystallite size.

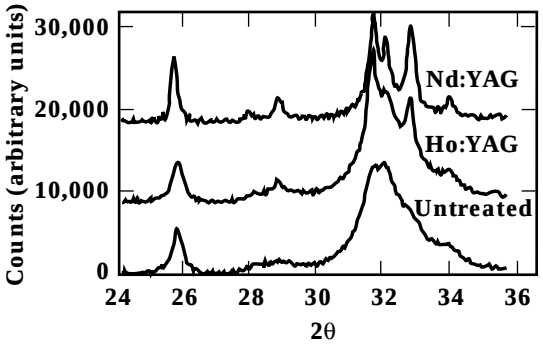
Applications

One of the most important uses of XRD is identification of compounds and phases on the basis of crystal structures. For example, XRD can be used for studies of phase transformations as functions of temperature and pressure. The technique very accurately measures atomic spacing in an easy, nondestructive manner. XRD is a powerful tool for characterizing structural properties such as strain state, defect structure, and crystallite size, by examining the peak broadening in the spectra. Another example is analysis of single crystals for orientation and unit cell size. Fiber textures can be identified in swage and forge-worked materials. Using glancing-angle XRD, surface contamination can be identified and monolayers and interfaces of multilayered films can be characterized.

As an example, XRD was used to analyze the effects of lasers on dentin etching. Laser irradiation alters the structure of dentin and produces surface layers that may be more resistant to demineralization. The morphological changes that occur in dentin when treated at two clinically interesting laser wavelengths was determined and the effectiveness of the laser-treated surface at resisting demineralization in an acid gel solution was evaluated. The Nd:YAG laser (wavelength 1060 nm) produced significant recrystallization and grain growth of the apatite without the formation of second phases such as β-tri-calcium phosphate. This recrystallized surface layer showed resistance to etching. The Ho:YAG laser-treated surface (wavelength 2100 nm) did not show significant evidence of recrystallization and grain growth, and only a trace amount of an acid-resistant layer was observed with etching.

Crystallite size measurements (Å) in untreated and irradiated dentin.

Sample	Crystallographic plane	
	[002]	[300]
Untreated	161.7 ± 4.1	80.8 ± 2.04
Nd:YAG	181.7 ± 7.6	151.7 ± 12.6
Ho:YAG	165.0 ± 5.0	101.7 ± 18.9



Superimposed x-ray powder diffraction patterns of untreated (control), Ho:YAG-lased, and Nd:YAG-lased dentin over a reduced angular range in 2θ. The laser-treated samples showed greater peak definition because grain growth occurred. No evidence for second-phase β-tri-calcium phosphate was observed.

Related Techniques

A number of complementary XRD techniques can be employed depending on sample type. Powder diffraction techniques include the goniometer method for identifying phases in excess of 1%, the Debye-Scherrer and Guinier methods for extremely small sample volumes, and the pole figure technique for determining the orientation texture of crystallites. Single-crystal methods include the Gandolfi method, a nondestructive diffraction technique for crystals less than 2 mm in size, and the Laue method for determining crystallographic orientations.

Sample Requirements & Analysis Time

The requirements, features, and limitations vary widely for the various analysis techniques used in XRD, as shown in the table below.

Instrumentation

Instrumentation includes four Philips XRG3100 generators with seven computer-controlled Norelco diffractometers and five Powder camera stations; two Philips 12045 generators with Laue and Read cameras; and one Rigaku Rotaflex generator with pole figure attachment, glancing angle attachment, and high-temperature attachment.

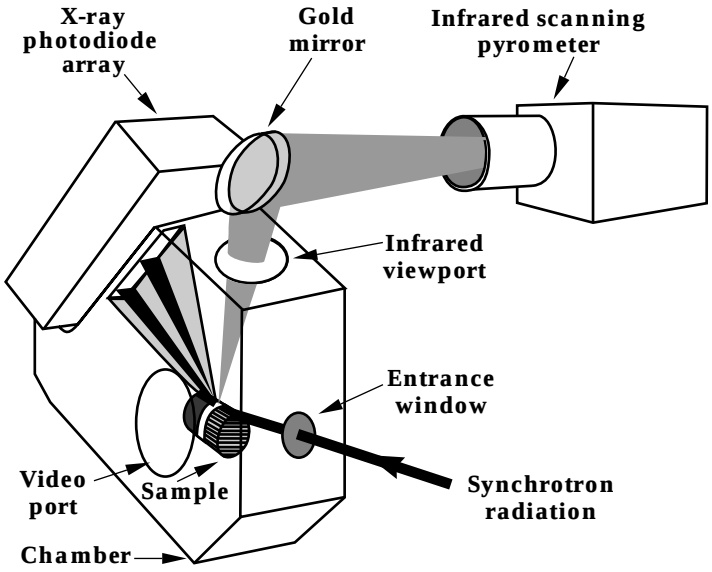
Sample requirements, analysis time, and features of XRD analysis techniques.

Analysis technique	Sample form	Sample size	Preparation	Data collection time	Data reduction time	Limitations	Output media	Unique features
Diffractometry	Powder or solid	0.1 mg (powder)–several mm (solid)	Some may be required	2–12 hr	1/2–1 hr	Detects only phases parallel to surface	Computer graphics w/ hard copy	Qualitative and semi- and quantitative analysis
Pole figure	Solid	3–20 mm diameter ~3 mm thick	Some may be required	1/2–3 hr	1/2–1 hr	Size of sample	Computer graphics w/ hard copy	Texture in oriented solids
Glancing angle	Solid	3–20 mm diameter ~3 mm thick	Some may be required	3–12 hr	1/2–1 hr	20–30°	Film	Thin films, epitaxy, and surface contamination
Debye-Scherrer	Powder	0.1–2 mg	Some may be required	5–8 hr	1/2–2 hr	Some materials not suited to film method	Film	Primarily quantitative
Guinier	Powder	2 mg	Minimum	1–2 hr	1/2–2 hr	—	Film	Precision lattice measurements
Read	Thin-film coatings	<50 mm	Minimum	2–8 hr	1/2–2 hr	Film may be too hard to read	Film	Texture in oriented solids
Gandolfi	Single crystal	50 µm–2 mm	Small crystals hard to mount	5–2 hr	1/2–2 hr	—	Film	Powder pattern from single crystal
Laue	Single crystal	200 µm–several cm	Minimum	5–50 min	1/2–2 hr	Film may be too hard to read	Film	Crystal-lographic orientation

Time-Resolved X-Ray Diffractometry

- **Real-time in situ monitoring of phase transformations and chemical dynamics**
- **Time resolution to milliseconds**
- **Simultaneous thermal history recording using scanning pyrometry**

A sample to be characterized by time-resolved x-ray diffractometry (TRXRD) is irradiated with narrow-bandwidth synchrotron x-ray radiation. The x rays diffracted by crystallites in the sample are detected by a photodiode array that records a powder diffraction pattern; an infrared scanning pyrometer records the temperature at the location of the x-ray beam on the sample surface. The data can be collected in an imaging mode (two-dimensional profile) with a 33-ms frame time and in a streak mode (one-dimensional profile) with a 125-μs time frame.



TRXRD for real-time, in situ monitoring of phase transformation and chemical dynamics of solid-state materials, with time resolution to milliseconds.

Applications

The use of synchrotron radiation as an analytical tool enables formerly difficult lab-based experiments to be done simply. For example, thin-film characterization and depth-dependent structural measurements are possible using synchrotron radiation and glancing angle x-ray diffraction. Time-resolved x-ray diffraction using synchrotron radiation can be applied to studies of reactions and phase changes.

As an example, we used TRXRD and scanning pyrometry to investigate the solid-state reaction of tantalum and carbon to form TaC and Ta_2C from mixed tantalum and carbon powders. We were able to clearly follow the reaction history as the reaction front passed the synchrotron beam.

Related Techniques

This technology offers capabilities that cannot be achieved by any other technique.

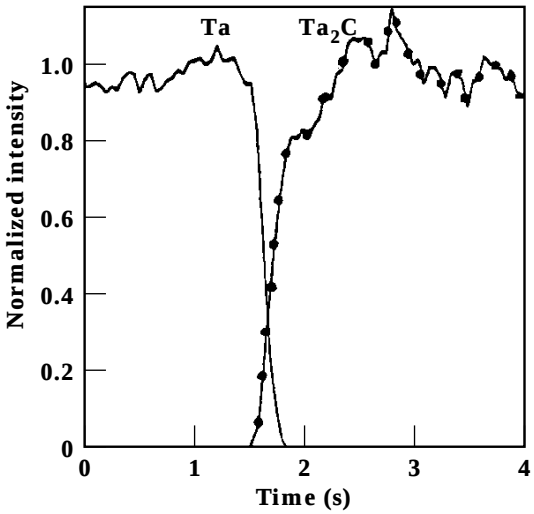
Sample Requirements & Analysis Time

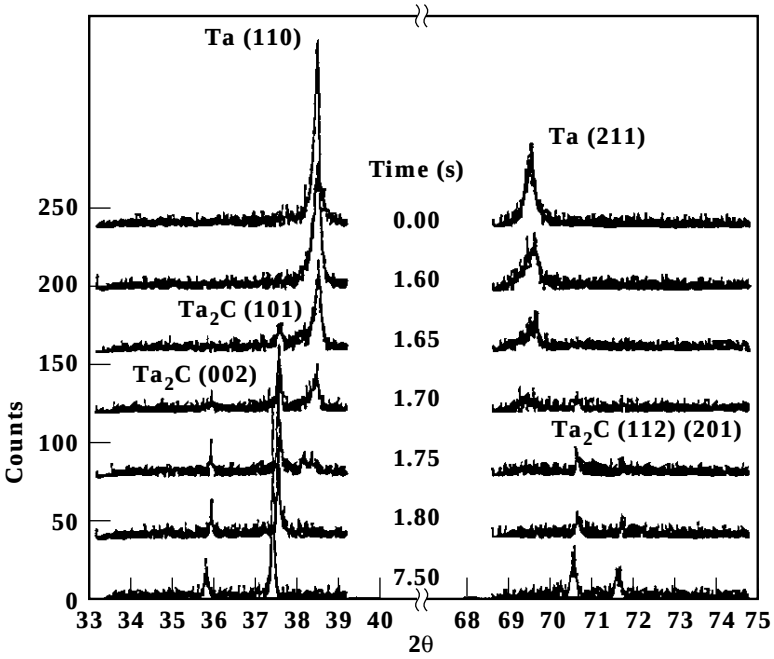
Experimental requirements vary, but phenomena occurring over a total time span of a few seconds to a few minutes can be investigated to a time resolution of a few milliseconds.

Instrumentation

The Chemistry and Materials Science Directorate operates and maintains beam-line facilities at the Stanford Synchrotron Radiation Laboratory in collaboration with a participating research team from the University of California. We also use

beam-line facilities at the National Synchrotron Light Source, and facilities are planned for the newly dedicated synchrotron sources at the Lawrence Berkeley Laboratory Advanced Light Source and at the Argonne National Laboratory Advanced Photon Source. Experimental samples to be probed may require some custom hardware and scheduling.





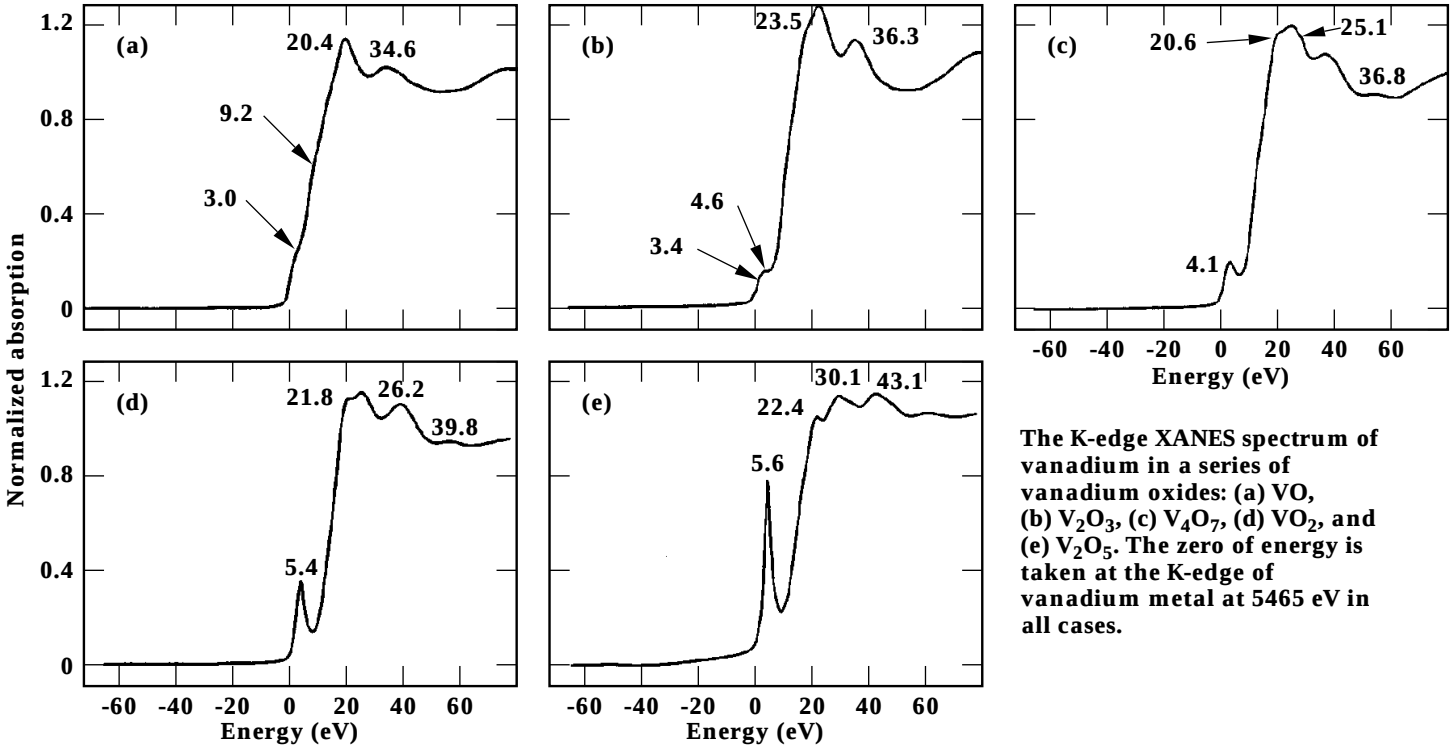
The TRXRD analysis of the synthesis of TaC: time-resolved diffraction patterns observed during synthesis (left), and normalized diffraction intensities of the tantalum, TaC, and intermediate Ta_2C phases as functions of time as the burn front propagates past the synchrotron beam (right).

Extended X-Ray Absorption Fine Structure & X-Ray Absorption Near-Edge Structure

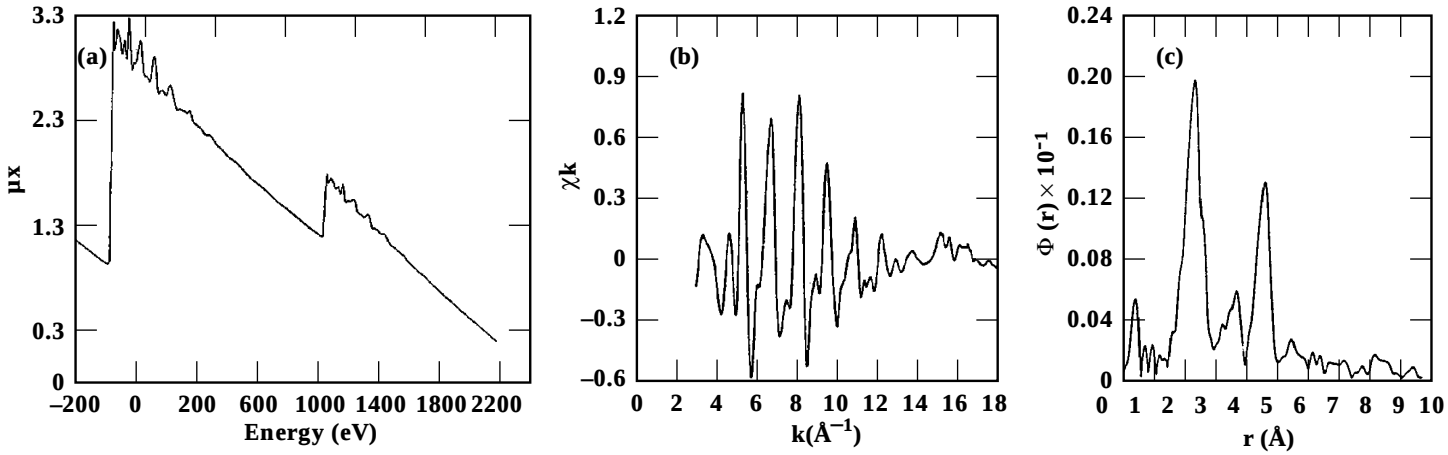
- **Determination of bond distances, coordination, and type of nearest neighbor atoms in ordered and disordered materials**
- **Identification of phases and compounds containing a specific element**
- **Orientation of adsorbed molecules on single-crystal surfaces**
- **Bonding and local structure of trace impurities in materials**
- **Quick-scan methods available**

In synchrotron x-ray diffraction, a sample is irradiated with a variable-wavelength synchrotron beam from an x-ray monochromator. The absorbed fraction of the incident x rays is monitored as a function of wavelength and, therefore, x-ray photon energy. The absorption can be measured directly from the transmission of the sample or inferred, often with higher sensitivity, from x-ray fluorescence or photoelectron yields. Each element in a sample has a set of characteristic x-ray absorption edges that provide the elemental specificity.

At x-ray energies just below each absorption edge is the near-edge structure caused by core-to-valence transitions. With x-ray absorption near-edge structure (XANES), the absorption edge identifies the valence of the element and gives information concerning its chemical coordination. Above it is a set of oscillations, or "fine structure," in the absorption that is caused by interference of photoelectron waves diffracted from neighboring atoms with the primary photoelectron wave. These oscillations are the basis for extended x-ray



The K-edge XANES spectrum of vanadium in a series of vanadium oxides: (a) VO, (b) V_2O_3, (c) V_4O_7, (d) VO_2, and (e) V_2O_5. The zero of energy is taken at the K-edge of vanadium metal at 5465 eV in all cases.



(a) Experimental EXAFS spectra above the K-edge of iron and nickel in a bcc iron–nickel alloy containing 80 at.% iron, (b) normalized EXAFS plotted as χk vs k in the nickel EXAFS, and (c) Fourier transform of (b) showing a shell-by-shell structure about the nickel central atom in the alloy.

absorption fine structure (EXAFS). Upon analysis, the oscillations can be isolated from the background and Fourier-transformed to obtain structural information.

Applications

EXAFS as well as XANES can be used to determine bond distance, coordination, and type of nearest neighbors about a given constituent atomic species in disordered systems such as glasses, liquids, solutions, and random alloys, or complex systems such as catalysts, biomolecules, and minerals. In ordered systems such as crystals and oriented surfaces, structural information on the next-nearest neighbors can also be obtained. In addition, it is possible to determine

- Structural evolution in amorphous-to-crystalline-transformation.
- Geometry of chemisorbed atoms or molecules on single-crystal surfaces.
- In situ, the structure of active sites in catalysts.
- In vivo, the structure of active sites in metalloproteins.
- Bonding and local structure of trace impurities in natural materials (e.g., coal) and synthetic materials (e.g., diamond).

Related Techniques

The x-ray or neutron diffraction can provide identification of bulk crystalline phases and average radial distribution functions of bulk amorphous phases, whereas EXAFS gives elementally specific bond lengths. The x-ray anomalous scattering also provides a nonelementally specific characterization of bulk amorphous materials.

Sample Requirements & Analysis Time

Samples can be solids, liquids, or gases. Ideally, solids should be thin foils or uniform films of fine powders that are 400 mesh or finer. Sample cross-section dimensions should be 5 × 25 mm at a minimum, and thickness should be 1 to 2 absorption lengths at the absorption edge of interest.

Scan times can take from a few seconds to several hours for dilute samples or surfaces. Spectrum analysis is done off-line and can take several hours or more.

Instrumentation

The Chemistry and Materials Science Directorate operates and maintains beam-line facilities at the Stanford Synchrotron Radiation Laboratory in collaboration with a participating research team from the University of California. We also use beam-line facilities at the National Synchrotron Light Source, and facilities are planned for the newly dedicated synchrotron sources at the Lawrence Berkeley Laboratory Advanced Light Source and at the Argonne National Laboratory Advanced Photon Source.

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In each laboratory, our specialists will help you obtain the most appropriate information for your needs.

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